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Enhanced Quantum Yield in Porphyrin Solar Cell with Redox Chain for Electron Transfer

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The Al/HD/MC/Au sandwich-type photovoltaic cell exhibits a relatively large photocurrent quantum yield of 39% at 445 nm when illuminated with the light of 21.5 μWcm^{-2} intensity at the Al/HD interface, where MC and HD represent 3-carboxymethyl-5-[(3-ethyl-2(3H)-benzothiazolylidine)ethylidene]-2-thioxo-4-thiazolidinone and a heterodimer consisting of 5,10,15-tri(4-chlorophenyl)-20-(3-pyridyl)porphyrin ($H_2pyp_3p(Cl)$) and 5,10,15,20-tetra(2,5-dimethoxyphenyl) porphyrinatozinc ($Zntpp(OMe)_2$), respectively.

The photovoltaic properties of porphyrin solids were so far considerably poorer than those of phthalocyanine and merocyanine because of the very large resistance ($\sim 10^{-13}$ Scm^{-1}) and the relatively large oxidation potential. We recently reported that, when a porphyrin heterodimer was used as a photosensitizer, larger photocurrent was obtained in the Al/porphyrin/Au sandwich-type solar cell because the porphyrin heterodimer acts as the special pair of the photosynthetic reaction center.[1] In order to improve further the photovoltaic properties, we tried to produce a redox chain for the electron transfer in the cell by mimicking a photo-reaction center of the photosynthesis. In this letter, we report first that the Al/porphyrin/MC/Au sandwich-type solar cells exhibit an enhanced photocurrent quantum yield compared with that of the Al/porphyrin/Au cells. In the Al/porphyrin/MC/Au cells, a redox chain is produced because the Al/porphyrin interface forms a MIS (Metal-Insulator-Semiconductor) type junction, and further MC is very easily oxidized in comparison with the porphyrins (the difference of the oxidation potentials is 0.3-0.6 V).[2] Then, we show that the cell

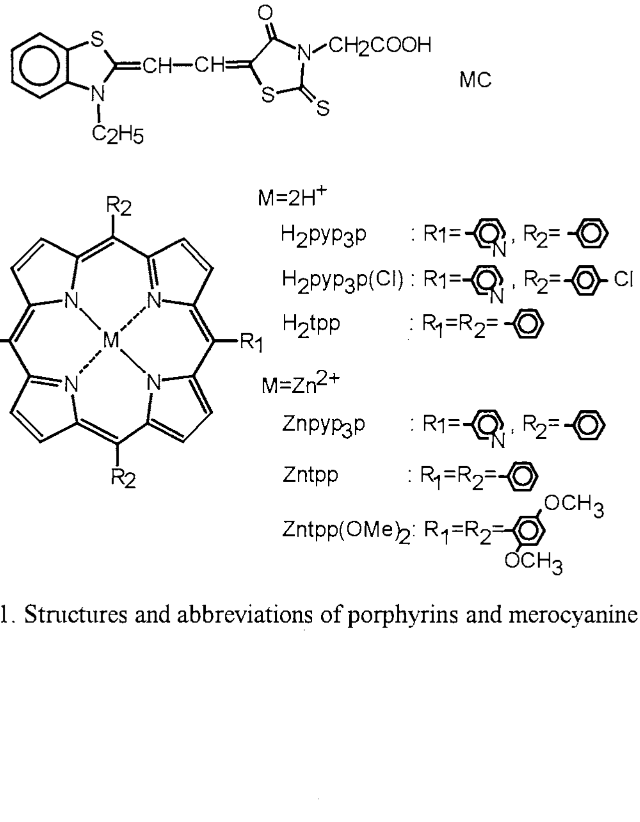

Fig. 1. Structures and abbreviations of porphyrins and merocyanine.

produced by combining above two ideas, using a porphyrin heterodimer as a sensitizer and MC as an electron donor, results in higher quantum efficiency.

Porphyrins and MC shown in Fig. 1 were synthesized and purified by literature methods.[3-6] Sandwich-type photovoltaic cells of Al/porphyrin/Au, Al/MC/Au, and Al/porphyrin/MC/Au were fabricated as in the previous paper.[7] The porphyrin and MC films were prepared by means of spin-coating and vacuum deposition onto an aluminum-coated glass substrate (transmittance at 500 nm is $20\pm5\%$). The photocurrent measurements were carried out as in the previous paper.[7]

It is known that pure porphyrin and MC solids behave as p-type semiconductors.[8, 9] Therefore, the photocurrent flowing from Au to Al is obtained in the external circuit of the photovoltaic cells, when illumination is performed from the Al/dye interface which forms a MIS-type junction. In all photocurrent measurements, a sample is illuminated from the active interface of Al/dye because the photocurrent remarkably decreases due to an optical filtering effect of the dye when illumination is carried out from the Au/dye interface.

The short-circuit-photocurrent quantum yield (ϕ_S) at Soret band of porphyrin solid for Al/porphyrin/Au and Al/porphyrin/MC(thickness, 20 nm)/Au cells is measured by using six kinds of porphyrins shown in Fig. 1. Figure 2 shows the dependence of ϕ_S value on the film thickness of porphyrin. The ϕ_S value increases by the deposition of MC on the porphyrins. However, the sandwich-type solar cell with the reverse sequence (Al/MC/porphyrin/Au) exhibits less ϕ_S value than that of the Al/porphyrin/Au cell. The results imply that, in the Al/porphyrin/MC/Au cells, the electron transfer from MC to porphyrin cation radical. which is produced by the electron injection from the excited porphyrin to Al, proceeds easily because the oxidation potential of MC is smaller than those of the porphyrins.[2] The larger increase of ϕ_S is obtained for the porphyrins with a pyridyl group such as H_2pyp_3p, $H_2pyp_3p(Cl)$, and $Znpyp_3p$ than for the porphyrins such as H_2tpp, Zntpp, and $Zntpp(OMe)_2$. Since the MC molecule is made up by the electron donor part such as thiazole ring and the electron acceptor part such as rhodanine ring, it has a large dipole moment.[10] The porphyrins with a pyridyl group also have a large dipole moment due to the unsymmetrical structure. Therefore, the two molecules interact electrostatically between their dipoles. Further, they can form a weak hydrogen bond between a carboxyl group in MC and a pyridyl group in the porphyrins. Due to these interactions at the porphyrin/MC interface, the rapid transfer of holes photogenerated in the porphyrin solid to the MC solid is achieved, and the large ϕ_S value is ultimately obtained in the Al/porphyrin with a pyridyl group/MC/Au cells.

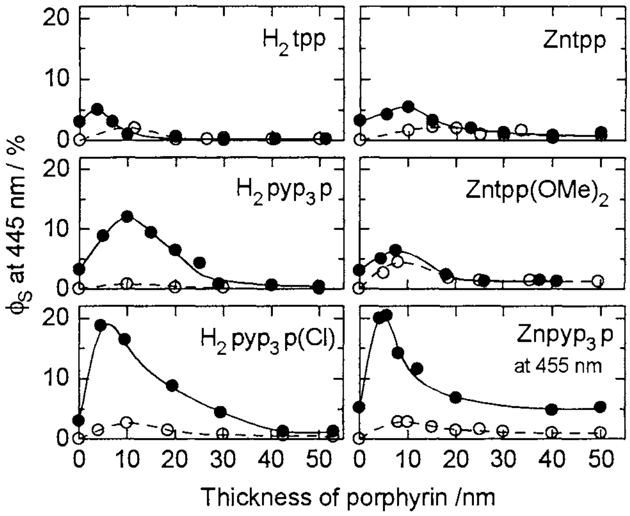

Fig. 2. Photocurrent quantum yield (ϕ_S) at Soret band of porphyrin solid for Al/porphyrin/Au (○) and Al/porphyrin/MC(20nm)/Au (●) cells as a function of the film thickness of porphyrin solid. The incident light intensity at the Al/porphyrin interface was 20 μWcm^{-2}.

Figure 3 shows the relation between the short-circuit-photocurrent quantum yield (ϕ_{445}) at the absorption peak of the film (445 nm) and the film thickness of HD solid for the Al/HD/Au cell, where HD indicates the equimolar mixed solid of $H_2pyp_3p(Cl)$ and $Zntpp(OMe)_2$. The ϕ_{445} value (○) is several times larger than the solar cells with pure porphyrin solids because of the formation of a ground-state complex by the axial coordination of a pyridyl group in $H_2pyp_3p(Cl)$ to the zinc ion in $Zntpp(OMe)_2$.[1)] The cell with the very thin HD film of 19 nm shows the maximum ϕ_{445} value of 26%. On the other hand, the nearly constant ϕ_{565} value of about 13% at 565 nm is obtained in the Al/MC/Au cell with the MC film from 10 nm to 50 nm. Since the photocurrent action spectra of Al/HD/Au and Al/MC/Au cells approximately fit in with the absorption spectra of the dye solids as shown in Fig. 4, it is found that the excited HD and MC molecules contribute to the photocurrent generation in the Al/HD/Au and Al/MC/Au cells, respectively.

In order to obtain larger photocurrent, it is required to achieve more effective charge separation at the Al/porphyrin interface. Therefore, we devise the Al/HD/MC/Au sandwich-type solar cell with two thin films of HD and MC. In fact, the very large ϕ_{445} value (● in Fig. 3) of 39% is given with very thin HD film of 10nm, but the sandwich-type solar cell with the reverse sequence (Al/MC/HD/Au) exhibits inferior photovoltaic properties as in the case of Al/MC/porphyrin/Au cells. The ϕ_{445} value of 39% implies that 62% of the photons absorbed to the dye films is transformed into photocurrent on the assumption that the ϕ value is proportional to light intensity, since the absorbance of the HD/MC films at 445 nm is 0.43. Such a large quantum efficiency is explained

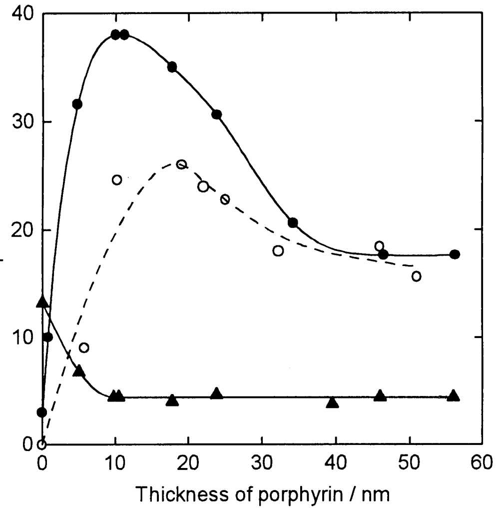

Fig. 3. Photocurrent quantum yield (ϕ) of Al/HD/Au cell at 445 nm (○), Al/HD/MC(20nm)/Au cell at 445 nm (●) and 565 nm (▲) as a function of the film thickness of HD. The light intensities of 445 nm and 565 nm at the Al/HD interface were 20 μWcm^{-2} and 30 μWcm^{-2}, respectively.

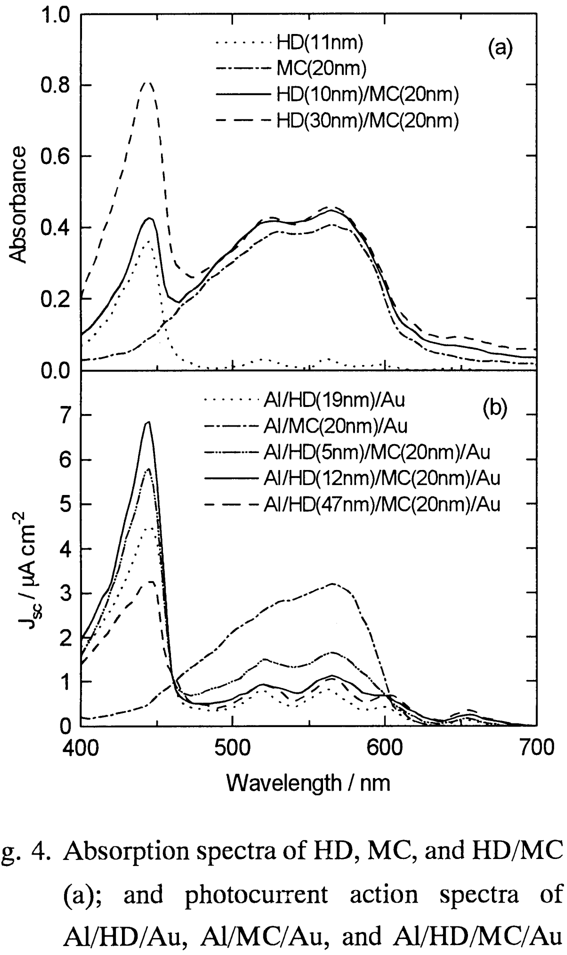

Fig. 4. Absorption spectra of HD, MC, and HD/MC (a); and photocurrent action spectra of Al/HD/Au, Al/MC/Au, and Al/HD/MC/Au with the incident light intensity of 50 μWcm^{-2} at the Al/dye interface (b). Thickness of the dye films was shown in the parenthesis.

as follows. Because the porphyrin heterodimer, which is similar to a special pair of the photosynthetic reaction center, has longer life time at the photoexcited state, many electrons and holes can be generated at the Al/HD interface. Then, rapid electron transfer from MC to HD cation like in photosynthesis effectively prevents the recombination of the electrons and holes. For the Al/HD/MC/Au solar cell, we obtain the open-circuit photovoltage (V_{OC}) of 0.77 V, the short-circuit photocurrent (J_{SC}) of 2.9 μAcm^{-2}, the fill factor (ff) of 0.19, and the energy conversion yield (η) of 1.9% when illuminated with 445 nm monochromatic light of 21.5 μWcm^{-2} intensity at Al/HD interface. Although the absorption spectrum of the HD/MC film coincides with the spectrum calculated by the simple summation of those of the HD and MC films, the photocurrent action spectra are similar to the absorption spectrum of HD film as shown in Fig. 4. This implies that the excited MC molecules only slightly take part in the photocurrent generation because the potential gradient in the MC solid is small due to the very narrow width of the space-charge layer at the Al/porphyrin interface (10–40 nm),[11] and simply act as an electron donor even in the Al/HD/MC/Au cell with very thin HD film. Only the excited HD molecules play an important role for the initial process of photocurrent generation. While, the ϕ_{565} value (▲ in Fig. 3) decreases with the increase in the film thickness of HD and reaches the value for the Al/HD/Au cell. Because the photon number absorbed at 565 nm by HD is less than that by MC due to the small absorption coefficient of HD, the shift of the space-charge layer from MC to HD by insertion of the HD between Al and MC causes the decrease of the photocurrent. In summary, a large quantum yield is obtained for the organic solar cell that imitates the photoreaction center of the photosynthesis.

References

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